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(54) Title: PROCESS FOR PREPARING A STABILIZED POLYESTER

(57) Abstract: The present invention discloses a process for preparing a stabilized polyester that is low in the generation of aldehydes wherein: a polyester is prepared by reacting one or more diacids with one or more diols in an esterification process, and/or one or more diesters with one or more diols in a transesterification process, and adding a phosphorus-containing stabilizer to a polyester between the end of the melt phase and prior to subsequent secondary melting of the polyester in processing to the final article such as a bottle, characterized in that the stabilizer comprises one or more tri(phenyl) phosphites, wherein each phenyl group independently contains at least one substituted ortho position and, optionally mixed with one or more phenolic antioxidants.

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## PROCESS FOR PREPARING A STABILIZED POLYESTER

Field of invention

The present invention relates to a process for preparing a stabilized polyester or copolyester. More in particular, the present invention relates to a process for preparing a stabilized polyester or copolyester based on one or more diacid components and one or more diol components. More in particular, the present invention relates to a process for preparing a stabilized polyester or copolyester that is low in the generation of aldehydes.

Background of the invention

International application WO 97/44376 concerns a continuous process for producing poly(ethylene terephthalate) polyesters ('PET') which is relatively free of acetaldehyde, wherein a stabilizer is added at or after the end of the polymerization reaction, but prior to polyester processing steps. The preferred stabilizer is ULTRANOX 626 (ULTRANOX is a trademark).

Unfortunately, the advantage of a low acetaldehyde generation, when this polyester is applied in the production of molded end products, is offset by a gray or black outward appearance (graying) of the polyester. In one particular field of application, the preparation of mineral water bottles, it is essential that the polyester that is used to prepare the bottles generates no or hardly any aldehyde during the molding of the bottle, but also allows the preparation of a bottle of high brightness and clarity. Mineral water sold in a slightly gray bottle will be less attractive to the customer and should hence be avoided. It is therefore desirable to provide a process for preparing a polyester that (upon

further processing) generates no more aldehydes than process described in the International application, but at the same time does not suffer from discoloration.

On the topic of stabilization there is extensive prior art. For instance, polyester resin compositions having excellent heat resistance, and superb toughness and abrasion and wearing resistance, are disclosed in European Patent Application No. 238,140 including the use of various phosphorus- and sulfur-containing antioxidants in combination with a phenolic antioxidant. Phosphorus-containing antioxidants suitable to the task mentioned are made of phosphorous ester, phosphonite, phosphophenanthrene, dioctadecyl pentaerythrityl diphosphite, trioctadecyl phosphite, tris(nonylphenyl)phosphite, tris(2,4-di-tert.butylphenyl)phosphite, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10 oxide and tetrakis(2,4-di-tert.butylphenyl)-4,4'-biphenylene diphosphite. However, this reference is in particular concerned with crystalline polyesters or polyester-polyolefin blends for use as ovenable trays. Such polyesters or polyester-polyolefin blends would not be suitable for bottle applications. Moreover, this reference does not address the problem of providing low aldehyde-generating polyesters that additionally have excellent brightness and clarity.

Stabilizer mixtures are also disclosed in UK Patent Application No. 2,311,528. The compositions therein disclosed comprise a specific organic phosphite (IRGAFOS 12, ex Ciba-Geigy) (IRGAFOS is a trademark) and a specific sterically hindered phenol, such as IRGANOX 1098, IRGANOX 1076, IRGANOX 1010, IRGANOX 245, IRGANOX 259, IRGANOX 1035, IRGANOX 3114 or IRGANOX 3125 (IRGANOX is a trademark). These stabilizer mixtures are used for stabilizing polyamide, polyester or polyketone polymers against oxidative, thermal and/or light-induced

degradation. Again, the problem underlying the present invention is neither mentioned nor solved.

#### Summary of the invention

5 The present invention provides a process for preparing a stabilized polyester or copolyester (hereinafter referred to as polyester) that is low in the generation of aldehydes wherein: a polyester is prepared by reacting one or more diacids with one or more diols in an esterification process, and/or one or more diesters  
10 with one or more diols in a transesterification process, followed by a melt phase polycondensation process, adding a phosphorus-containing stabilizer to a polyester between the end of the melt phase and prior to subsequent secondary melting of the polyester in processing to the  
15 final article such as a bottle, characterized in that the stabilizer comprises one or more tri(phenyl) phosphites, wherein each phenyl group independently contains at least one substituted ortho position and, optionally mixed with one or more phenolic antioxidants.

#### Detailed description of the invention

20 The preparation of polyesters (that is again to refer to both polyesters and copolyesters) is known. Typically, the preparation involves catalyzed esterification of one or more diacids with one or more diols, and/or by  
25 transesterification of one or more diesters with one or more diols. The polyesters so produced may be used directly, but are more commonly subjected to a subsequent solid state polycondensation step to increase their molecular weight.

30 Common samples of diacids used in the preparation of polyesters include (cyclo)aliphatic diacids and/or aromatic diacids. For instance, diacids containing up to 40 carbon atoms may be used.

35 Suitable aliphatic diacids are for instance oxalic acid, malonic acid, dimethylmalonic acid, succinic acid,

pimelic acid, adipic acid, trimethyladipic acid, sebacic acid, azelaic acid, dimeric acids (dimerization products of unsaturated aliphatic carboxylic acids such as oleic acid) and alkylated malonic and succinic acids such as octadecylsuccinic acid.

Suitable cycloaliphatic diacids include 1,3-cyclobutanedicarboxylic acid, 1,3-cyclopentanedicarboxylic acid, 1,3- and 1,4-cyclohexanedicarboxylic acid, and the like.

In particular aromatic diacids based on benzene, substituted benzenes, fused polycyclic hydrocarbons and substituted versions thereof have been used in the preparation of commercial polyesters. Examples of suitable aromatic diacids include PTA (pure terephthalic acid), IPA (isophthalic acid), and other aromatic diacids such as o-phthalic acid, 1,3-, 1,4-, 2,6- or 2,7-naphthalene dicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenylsulfonedicarboxylic acid, 4,4'-benzophenonedicarboxylic acid, 1,1,3-trimethyl-5-carboxyl-3-(p-carboxylphenyl)indane, 4,4'-diphenyl ether dicarboxylic acid, bis-(p-carboxylphenyl)methane or bis(p-carboxylphenyl)ethane. The preferred diacids used in the process of the present invention are PTA and IPA.

The aforementioned diacids may also be used in various combinations. A combination of diacids that has been found to be very suitable comprises PTA containing 1-10, preferably 1.5-7.5 mol% IPA (calculated on total diacid component).

Instead of, or in addition to the diacid(s) mentioned above, various diesters may be used. For instance, diesters that correspond in respect of their acid moiety to the aforementioned diacids may be used. Suitable diesters therefore also include the aliphatic and the aromatic kind. Very suitable diesters are for instance the esters of PTA and IPA, and esters of naphthalene dicarboxylic acid. The alcohol moieties of the diesters

are typically based on an alkanol having 1 to 4 carbon atoms in the molecule, and/or correspond to the diol defined hereafter.

5 A wide variety of diols (also referred to as glycols) may be used in the preparation of polyesters. These may comprise aromatic backbones or aliphatic backbones; may comprise short backbones (e.g., as in monoethylene glycol) or long backbones (e.g., hydroxy-terminated polyolefins or polydienes or the like); and may be  
10 straight-chained (e.g., 1,6-hexanediol) or branched (e.g., 1,2-propanediol). The diol may also contain one or more non carbon atoms in its backbone, for instance in the form of one or more ether groups (e.g., diethylene glycol).

15 Suitably the diol is selected from one or more alkanediols having 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms in the molecule and/or the condensed products (ethers) thereof. The diol most frequently used in the preparation of polyesters is MEG (monoethylene glycol), optionally in admixture with DEG (diethylene glycol) and/or other diols. Other diols that have been  
20 used before include for instance 1,3-propanediol, 1,2-, 1,3- or 1,4-butanediol, (substituted) cyclobutane diol(s), 1,6-hexanediol, 1,6-cyclohexanediol, poly(alkylene glycol), etc.

25 It is also possible that the polyesters contain small amounts, e.g., for 0.1 to 3 mol% of a polyfunctional comonomer.

30 Bottles are typically made from polyesters wherein PTA comprises at least 80 mol% of the diacid component, and MEG comprises at least 80 mol% of the diol component. The present invention is particularly applicable in respect of such polyesters (herein after collectively referred to as PET). These polyesters may suffer from the  
35 generation of AA (acetaldehyde).

The graying of polyesters, and PET in particular, is related to the phenomenon of catalyst reduction into a reduced state or even its elemental state. The most common polycondensation catalysts are composed of or comprise antimony compounds. Upon contact with a phosphite or similar reductor, these antimony-based catalysts revert into microscopic metal particles that turn the polyester black. Other metals used in catalyst systems include cobalt, zinc, magnesium, manganese, calcium and titanium.

The formation of minute amounts of metal particles is harmless or even desirable (as black body to increase IR heat-up rates of the polyester). But the presence of such particles, if any, should not effect the clarity of the polyester so produced, and should certainly not be visible.

Polyesters, as is explained in WO 97/44376, may be produced in a conventional batch process, wherein the product of the transesterification or esterification is formed in one vessel and then transferred to a second vessel for polymerization. The second vessel is agitated and the polymerization reaction is continued until the power used by the agitator reaches a level indicating that the polyester melt has achieved the desired intrinsic viscosity ('IV') and therefore, the desired molecular weight. For instance, in the preparation of PET, the (trans)esterification is typically conducted at an elevated temperature (e.g. 200 to 350 °C), to produce a polyester having an IV of 0.3 to 0.8 dl/g, commonly about 0.6 dl/g (as determined by ASTM D-4603-86, at 30 °C in 60/40 w/w phenol/tetrachloroethane).

Alternatively, these steps may also be carried out in a continuous process. For instance, the continuous process described in WO 97/44376 is conducted by combining the diol with the diacid or diester

(hereinafter the reactants) at a temperature of about 240 to 290 °C and at a pressure of from about 30 to 600 kPa for about 1 to 5 hours to yield low molecular weight oligomers and water. In general, a continuous feed of reactants is used employing a molar ratio of diol to diacid or diester of from about 1.0 to 1.6. The reaction is typically uncatalyzed. The water or alcohol so produced is removed as the (trans)esterification reaction proceeds.

In the second stage of the continuous process, which is a polycondensation stage generally conducted in a series of 2 or more vessels, the oligomers are agitated at a temperature of about 260 to 305 °C for about 1 to 4 hours in the presence of a polymerization catalyst to form the polyester melt.

Typically, the polycondensation reaction begins in a first vessel operated at a pressure range of from about 0 to 10 kPa. Diol produced in the polycondensation is removed from the polyester melt using an applied vacuum. The polyester melt is typically agitated to allow the diol to escape from the polyester melt.

As the polyester melt is fed into successive vessels, the molecular weight and thus the IV of the polyester melt increases. The temperature of each vessel is generally increased and the pressure decreased to allow greater polymerization in each successive vessel. The final vessel is generally operated at a pressure of from about 0 to 5.5 kPa. Each of the polymerization vessels communicates with a flash vessel. The retention time in the polymerization vessels and the feed ratio of the reactants into the continuous process are determined in part based on the target molecular weight of the polyester.

The polymerization catalyst employed in the continuous process is generally added prior to, at the start of, or during the polycondensation stage.

When the polymerization process is completed, the resulting polyester, which is still in the form of a melt, is generally filtered and then typically extruded and pelletized before being worked up into specific polyester articles or injection molded in a preform or coating into an item such as a bottle. Such steps are also typically labeled as "polyester processing" but refer of course to later working of the finished polyester rather than to the chemical processing steps used to form the polyester in the first place.

For instance, polyester melt may be extruded into polyester sheets, filaments, pellets, chips or similar particles (so-called primary extrusion step). Preferably, the polyester melt is extruded shortly or immediately after exiting the polycondensation stage, whereupon it is quenched, for instance in a water trough or alternative cooling unit. The formation of pellets or chips is particularly convenient for storage, transport and handling purposes.

The pellets or chips may be subjected to solid state polymerization (SSP), for instance, to raise the IV to 0.7 to 1.2 dl/g, preferably to about 0.8 dl/g.

In order to produce the final polyester articles, in the form of bottles, filaments, sheets, molded articles and the like, the pellets or chips are re-melted and re-extruded (so-called secondary extrusion step).

According to the present invention, the stabilizer may be injected into the polyester melt or during the secondary melting of the polyester. The resulting polyester melt may then be extruded through a die following the polymerization. The stabilizer may also be added when the polyester melt is being extruded, by using

a screw extruder or similar means. Preferably, the stabilizer is added at any point to the melt polymer but preferably during the primary extrusion and/or during the secondary extrusion of the polyester.

The extrusion conditions are conventional. For instance, the polyester may be extruded at a temperature in the range of 240 to 315 °C.

The stabilizer is advantageously used in an amount of at least about 0.05% (weight on weight, based on the weight of the stabilizer and the polyester). The stabilizer may be added up to an amount of 20 %w/w. Higher amounts may be used, but will not necessarily achieve better results. Rather, the stabilizer is preferably used in a range of about 0.05 to about 1.0 %w/w, preferably in the range of about 0.1 to about 1.0 %w/w when the stabilized polyester is to be ready for further processing; or the stabilizer is preferably used in a range of about 5.0 to 15.0 %w/w, preferably in the range of about 6.0 to about 12.5 %w/w when the stabilized polyester is used as a 'master batch' for addition to another (e.g., not stabilized) polyester batch. In the latter embodiment, the master batch may be mixed with the main polyester batch prior to further processing in the form of injection molding or in the secondary processing step. This main polyester batch need not be a similar polyester, nor need it have the same molecular weight. Rather, it is an advantage of the present invention that the main polyester batch can be solid state polymerized according to conventional procedures.

The stabilizer, as is indicated above, is actually a mixture of one or more phosphites with, optionally, one or more phenolic antioxidants. If the phosphite is not a tri(phenyl)phosphite, wherein each phenyl group independently contains at least one substituent on the ortho position, then the moldings of the polyester turn

gray or black. Surprisingly, we have found that the addition of the stabilizer as defined herein does not produce excessive discoloration when added according to the invention. Preferably, the or each substituent attached to the phenyl groups is a secondary or preferably tertiary alkyl group. Particularly suitable are tertiary butyl groups of which there may be one, two or three per phenyl group. One or more of the phenyl groups may contain an additional phosphite group, provided this phosphite group is also a tri(phenyl)phosphite wherein each phenyl group independently contains at least one substituent on the ortho position. Two or more of the phenyl groups may be linked. The preferred phosphite is tris(2,4-di-tert.butylphenyl)phosphite (IRGAFOS 168, sold by Ciba-Geigy).

The phenolic antioxidant useful in the practice of this invention is a hindered phenolic compound in which a bulky group is contained at a position ortho to the OH group of the phenolic compound. Specific examples of the hindered phenolic compound include 2,2'-methylene-bis(4-methyl-6-t-butylphenol), 4,4'-butylidene-bis(3-methyl-6-t-butylphenol), tetrakis[methylene-3-(4'-hydroxy-3',5'-di-t-butylphenyl)propionate]methane (IRGANOX 1010), n-octadecyl-3-(4"-hydroxy-3',5'-di-t-butylphenyl)propionate (IRGANOX 1076), 2,4-bis(octylthio)-6-(4'-hydroxy-3',5'-di-t-butylanilino)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-tris(3'-hydroxy-2',6'-dimethyl-4'-t-butylbenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, and 1,3,5-trimethyl-2,4,6-tris(4'-hydroxy-3',5',-di-t-butylbenzyl)benzene. These phenolic antioxidants may be used alone or in combination. The preferred antioxidant used in the process of the present invention may be any one of the sterically hindered phenols described in UK patent application No. 2,311,528, that is incorporated herewith

by reference. For instance, good results have been achieved with IRGANOX 1010 and IRGANOX 1076, in particular the former phenolic antioxidant.

When used together, the phenolic antioxidant and the phosphite may be used at various ratios. Suitable results have been achieved in a ratio of antioxidant to phosphite of 10:1 to 1:10, preferably in a ratio of 6:1 to 1:6. Use of excessive phenolic antioxidant may have an adverse "yellowing" effect on the color of the molded polyester.

In addition to the phosphite and phenolic antioxidant, the polyesters of the present invention may contain various additional additives or co-stabilizers. For instance, they may contain UV absorbers and light stabilizers, nucleating agents, fillers and reinforcing agents, fast heat-up additives (e.g., carbon black), plasticizers, lubricants, emulsifiers, neutralizing agents, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents. These additives may be used at various amounts, ranging from ppb to pph level, typically less than 0.5 %w/w (on total polymer).

When the process of the present invention involves the preparation of a masterbatch, and the subsequent addition of the masterbatch to an untreated polyester, then preferably a neutralizing agent is added. Thus, some yellowing occurs in preforms made from a masterbatch and an untreated polyester when the masterbatch is made without proper drying of the polyester component it is made of. The properties of the masterbatch are restored by the addition thereto of for instance a hydroxytalcite. Good results have been achieved with synthetic hydroxytalcites, e.g., DHT-4A (DHT is a trademark), commercialized by Kyowa Chemical Industry Co. Ltd., and described in GB-A-2,075,989 (the content of which is

incorporated herewith by reference). Alternative neutralizing agents that may have a similar effect include stearate salts (e.g., calcium stearate) and the like.

5           The amount of neutralizing agent used may vary widely, depending on the occurrence of the yellowing phenomenon. For instance, the synthetic hydroxycalcite may be used in an amount varying from 0.1 to 2.0 %w/w on the total masterbatch.

10           The polyesters produced according to the present invention are particularly suitable for the preparation of mineral water bottles. However, they may find application in films, trays, containers of various forms, (baby) toys, (automobile) wind shields and other  
15           appliances where clarity and low aldehyde generation are desired.

          The present invention will be illustrated by the following examples. In the examples the intrinsic viscosity is determined by the ASTM method described  
20           above. The abbreviations used in the examples are set out in the following table:

P58, P60, P76, P80	poly(ethylene terephthalate) copolyesters containing minor amounts of incorporated isophthalic acid (less than 3 mol%), having an IV of about 0.58; 0.60; 0.76 or 0.80 dl/g
U626	bis(2,4-di-tert.butylphenyl)pentaerythritol diphosphite, ULTRANOX 626
TNPP	tri(nonylphenyl)phosphite
I1010	tetrakis[methylene(3,5-di-tert.butyl-4-hydroxyhydrocinnamate)methane], IRGANOX 1010
I1076	octadecyl 3(3,5-di-tert.butyl-4-hydroxyphenyl)propanoate, IRGANOX 1076
il68	tris(2,4-di-tert.butylphenyl)phosphite, IRGAFOS 168
B561	4:1 w/w blend of I168 and I1010, IRGANOX B561
B900	4:1 w/w blend of I168 and I1076
E398	2,2'-ethylidene-bis(4,6-di-tert.butylphenyl)-fluorophosphite, ETHANOX 398 (ETHANOX is a trademark)
il12	2,2',2''-nitrilo triethyl-tris[3,3',5,5'-tetra-tert.butyl-1,1'-biphenyl-2,2'diyl]phosphite, IRGAFOS 12
AA	acetaldehyde

### Examples

#### (a) Powder mixing

In one series of experiments, P60 was dried and passed through a co-rotating twin screw extruder (made by Werner & Pfleiderer) operating at 255-260 °C and 10 kg/h. Powdered additives were dry blended with P60 powder and dosed to the melt in the extruder at a point close to that where the melt left the extruder as strands which were chopped to granules. The granules were dried and then converted to 50 g preforms on a Netstal HP1200 injection molding machine in a two-cavity mold.

When various phosphorus containing compounds were added at 0.2% level on final polymer, preforms with the following appearances resulted (opaqueness believed due to the powder):

Additive	Appearance
U626	opaque, grey
TNPP	opaque, grey
B561	opaque, white
No additional compound	opaque, white

5     **(b) Powder/granules mixing**

The experiments described in (a) were repeated, except that the additive was intimately mixed with the granules added to the drier and fed to the extruder, and no powder was added separately along the extruder. In one  
10     experiment where 0.2% of B561 was used as additive, the resultant preforms were colorless and contained 4.8 mg/kg of acetaldehyde.

In a comparative experiment, in which no additive was included in the PET granules added to the extruder, the  
15     preforms were colorless and contained 6.8 mg/kg of acetaldehyde.

In a further comparative experiment, in which the B561 was substituted by a 4:1 weight ratio blend of I12 and I1010, the preforms were grey and contained 6.4 mg/kg  
20     acetaldehyde.

**(c)**

In a further series of experiments, the conditions of paragraph (a) were used, except that the granules were subjected to a solid state polymerization to increase  
25     their intrinsic viscosity to about 0.78 dl/g. On injection molding these gave preforms of the following

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properties as a function of the phosphorus containing additive used:

Additive	Appearance
U626	transparent, dark gray, 5.2 mg/kg acetaldehyde (color unacceptable for normal bottles)
TNPP	transparent, gray, 4.6 mg/kg acetaldehyde (color unacceptable)
E398	transparent, light yellow, 5.4 mg/kg AA
I561	transparent, pale yellow (acceptable), 3.8 mg/kg AA
none	transparent, colorless and contained 6.9 mg/kg AA

(d)

5 In another series of experiments, P58 granules were  
dried and fed at 70 kg/h to a single screw extruder. 10%  
of the stream emerging from the extruder was diverted to  
a twin screw extruder, where additive powders were dosed  
from a K-tron loss in weight feeder (or no additive in  
case of the comparative example) before the diverted  
10 stream was re-united with the main stream and passed  
through a static mixer before passing as strands through  
a water bath and granulation. The granules so obtained  
were solid state polymerized at 226 °C under vacuum to  
0.72 dl/g IV, and converted to preforms on an Arburg All-  
15 rounder single cavity injection molding machine. The  
color of the preforms was measured using a Hunter  
colorimeter. The results of the measurement give an L\*  
rating (lower L\* value = grayer preform). The following  
results were obtained:

Additive	Preform L*	Preform AA (mg/kg)
0.1% B561	77.5	5.7
0.2% B561	76.0	5.8
0.1% B900	78.4	7.1
0.2% B900	77.6	5.4
none	79.0	6.9

N.B. the lowest values of L\* found here still give bottles of highly acceptable appearance.

(e) Component ratios

The following series of experiments demonstrate that a range of ratios between the substituted tri(phenyl)phosphite and phenolic antioxidant may be employed. The additives were dry blended as powders with dried granules of commercially available CLEARTUF P58 bottle resin (CLEARTUF is a trademark), and the mixture put into the hopper of a Leistritz twin screw extruder and passed through the extruder and granulated. The extruder temperature profile was 280 °C in melting zones, and reduced to about 250 °C just prior to exiting the die. The pellets thus obtained were subjected to solid state polymerization as in (d) above, and similarly converted to preforms. The preforms were blown into bottles and head space acetaldehyde concentration determined after purging with nitrogen, one hour after blowing, then capping and storage for 24 hr at 21 °C. The results demonstrate a general deterioration in resin color as I1010 increases in the mixture. (Higher b\* value = more yellow.)

Additive	SSP resin color b*	Preform AA content mg/kg	Bottle AA content µg/l	Bottle color b*
none	-0.46	6.4	2.3	2.5
none, duplo	1.75	6.6	2.3	1.7
0.1 %w i168	-0.86	4.9	1.7	2.2
0.1 %w 6:1 i168:I1010	-0.02	5.2	1.9	1.2
0.1 %w 4:1 i168:I1010	-0.63	5.4	1.8	1.2
0.1 %w 1:1 i168:I1010	0.74	4.5	1.7	1.3
0.1 %w 1:6 i168:I1010	1.59	5.4	1.8	1.6
0.1 %w I1010	0.44	5.2	1.9	1.3

(f) MB experiments (i)-(v)

(i) A masterbatch (containing 12% 6:1 w/w i168 + I1010) was produced by adding the additives through the mid-point feeder system of a Leistritz twin-screw extruder whilst extruding and granulating a dried, commercially available PET bottle resin CLEARTUF P76. The masterbatch was dried at 100 °C, and mixed into dried commercially available bottle resin CLEARTUF P82 fed to a Netstal 35000 injection molding machine equipped with a 48 cavity preform mold, such that the additive concentration in the final product was 0.2 %w. The heaters along the barrel of the injection molding machine were set at 235-240-258-270-270-270 °C from hopper to nozzle. 41 gram preforms were produced having an IV of 0.758 and 2.2-2.5 mg/kg acetaldehyde content.

(ii) In a comparative experiment in which no masterbatch was added to the P82, the same preforms were

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produced, having an IV of 0.757 dl/g and an acetaldehyde content of 4.2-4.7 mg/kg.

(iii) However, the preforms had a slight yellow-brown appearance when the experiment was repeated with undried P76, and the produced masterbatch as well as the bottle resin P82 were dried under air for 8 hours before the preparation of the preforms.

(iv) This discoloration phenomenon did not occur, even on prolonged drying, when this experiment was repeated (iv) with a masterbatch made by adding 12% 6:1 w/w i168 + i1010 and 0.5% DHT-4A.

(v) Addition of the masterbatch described in (i) to a polyester containing 5.3 mol %wt copolymerized IPA, and 1 mg/kg carbon black resulted in a reduction of acetaldehyde content from 2.0-2.5 mg/kg to 1.0-1.4 mg/kg.

g) stabilizer addition during PET polymerization

A series of P60 polyesters were produced in a 90 kg bench scale/pilot plant reactor composed of two polycondensation vessels (S/1 and S/2). The polyesters were made of monoethylene glycol as diol and pure terephthalic acid containing 2,5 mol% isophthalic acid as diacid at a 1.1 molar ratio. Antimony acetate, dissolved in MEG was used as catalyst (added at S/1) and phosphoric acid was added to the second vessel (S/2).

In experiment 1 (the control) no stabilizers were added. In experiments 2 and 3 the stabilizers B561 or B900 were added either to vessel S/1 or S/2 in an amount of 0.2 %wt. The batch temperature range was 255-260 °C.

It was observed that the antimony catalyst precipitates with the phosphite stabilizers. When the stabilizers were added to vessel S/1, the 20 µm filters employed after S/1 became plugged. Moreover, long reaction times were observed.

Precipitation and reduction in reaction time also occurred during addition of the stabilizers to S/2. Color of the polyester was unacceptable. The results are set out in the following table.

Sample	IV	COOH	MP, °C	Tg, °C	DEG, wt%	L*	b*
#1, Control	0.623	29	249.8	77.4	1.59	68.8	0.8
#2, B561	0.608	20	249.4	78.0	1.63	51.4	-1.1
#3, B900	0.601	25	249.4	78.0	1.73	50.7	-0.9

5 The three batches were solid state processed for about 7.5 hours until an IV of about 0.74. These polyesters were then used in the production of (54 g) preforms and 2 litre bottles. Their properties are set out in the following table:

Sample	2 litre Bottle			54 g Preform		
	L*	b*	haze, %	L*	b*	haze, %
#1	91.1	2.08	1.86	80.93	7.7	44.82
#2	89.4	2.49	3.21	56.39	9.20	50.5
#3	88.7	2.64	4.12	54.88	9.75	51.91

10 As is obvious from the above, the clarity and color of the bottles and preforms are compromised when the additives are introduced at an early stage during the polymerization.

C L A I M S

1. A process for preparing a stabilized polyester that is low in the generation of aldehydes wherein:

5 a) a polyester is prepared by reacting one or more diacids with one or more diols in an esterification process, and/or one or more diesters with one or more diols in a transesterification process,  
b) adding a phosphorous-containing stabilizer to a melt of the polyester of step a) at or after the end of the (trans)esterification process of step a) and prior to  
10 subsequent processing of the polyester, characterized in that the stabilizer comprises one or more tri(phenyl)phosphites wherein each phenyl group independently contains at least one substituent on the ortho position.

15 2. The process of claim 1 wherein the stabilizer comprises a mixture of said tri(phenyl) phosphite with one or more phenolic antioxidants.

3. The process as claimed in claim 1, wherein the polyester comprises at least 80 mol% of terephthalic acid  
20 as diacid component and/or at least 80 mol% of monoethylene glycol as diol component.

4. The process as claimed in claim 3, wherein the polyester comprises 90 to 99 mol% of terephthalic acid and 10 to 1 mol% of isophthalic acid as diacid component.

25 5. The process as claimed in claim 1, wherein the stabilizer is added during an extrusion step.

6. The process as claimed in claim 1, wherein the stabilizer is added in an amount of at least about 0.05% by weight on weight (w/w), based on the weight of the  
30 stabilizer and the polyester.

7. The process as claimed in claim 1, wherein the stabilizer is added in the form of a polyester master batch.

8. The process as claimed in claim 7, wherein a neutralizing agent is added to the polyester master batch.

9. The process as claimed in claim 8, wherein the neutralizing agent is a hydroxytalcite, and the hydroxytalcite is added in an amount of 0.1 to 2.0 %w/w on the polyester master batch.

10. The process as claimed in claim 1, wherein the or each substituent attached to the phenyl groups of the phosphite is a secondary or tertiary alkyl group.

11. The process as claimed in claim 10, wherein the phosphite is tris(2,4-di-tert.butylphenyl)phosphite.

12. The process as claimed in claim 2, wherein the phenolic antioxidant used together with the phosphite is a sterically hindered phenol.

13. The process as claimed in claim 12, wherein the sterically hindered phenol is IRGANOX 1076 or IRGANOX 1010.

14. The process as claimed in claim 2, wherein the phenolic antioxidant and the phosphite are present in a ratio of antioxidant to phosphite of 10:1 to 1:10.

15. A stabilized polyester that is low in the generation of aldehydes that is prepared by a process wherein:

- a) a polyester is prepared by reacting one or more diacids with one or more diols in an esterification process, and/or one or more diesters with one or more diols in a transesterification process,
- b) adding a phosphorous-containing stabilizer to a melt of the polyester of step a) at or after the end of the (trans)esterification process of step a) and prior to subsequent processing of the polyester, characterized in that the stabilizer comprises one or more tri(phenyl)-

phosphites wherein each phenyl group independently contains at least one substituent on the ortho position.

16. Mineral water bottles, films, trays, containers, baby toys, and automobile wind shields prepared from a polyester as prepared in claim 1.

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## INTERNATIONAL SEARCH REPORT

Int. l. Application No.

PCT/EP 00/04911

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/526 C08K5/13 C08L67/02 C08J3/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JOB J. ZEILSTRA: "Heat stabilisation of segmented copoly(ether)esters" ANGEWANDTE MAKROMOLEKULARE CHEMIE. APPLIED MACROMOLECULAR CHEMISTRY AND PHYSICS., vol. 137, 1985, pages 83-92, XP002146518 WILEY VCH, WEINHEIM., DE ISSN: 0003-3146 page 91; table 3 ---	1,2,10, 12,14
A	EP 0 251 712 A (POLYPLASTICS CO) 7 January 1988 (1988-01-07) table 2 ---	1,2,10, 12-14
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Int. l. Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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